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Final Report
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Oxidation Resistance of CVD Coatings

February 1987

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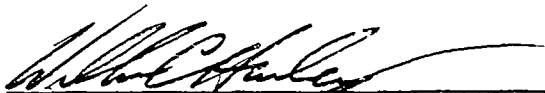Edwards Air Force Base,
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FOREWORD

This final report describes the work accomplished by Ultramet under contract F04611-84-C-0043 with the Air Force Rocket Propulsion Laboratory (AFRPL), Edwards Air Force Base, CA. AFRPL Project Manager was Kurt Chandler.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the DD Form 1473.

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Chemical vapor deposition (CVD) of (Ir), (Pt), (Rh), (ZrO$_2$), and (HfO$_2$) was investigated for the purpose of protecting Re, (Mo), Ni, Nb, (Cu) and carbon composites from oxidation at temperatures from 1000 to 2000°C. Iridium has proved easiest to deposit. Earlier difficulties with codeposition of carbonaceous residues were overcome, and dense, adherent, coatings which stop oxidation of the substrate are reliably produced. The iridium deposition process developed here was applied in the fabrication of several rhenium thrusters. Some of these have been test fired by Aerojet Techsystems using MMH/NTO propellant. One chamber has completed over 8 hours of operation including over 3600 starts and 4 hours burn time between 2150 and 2200°C at a mixture ratio of 1.65. No measurable change in throat diameter was observed and the mass loss was only 0.9 g or 1.4%. (Keywords:)

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TABLE OF CONTENTS

LIST OF FIGURES

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iii

INTRODUCTION

Increased efficiency as well as reduction in mass and size can be achieved for rocket engines and gas turbines by operating at higher temperatures. Examples include the JPL fluorine/hydrazine thruster development program with throat temperatures in the 1500°C to greater than 2000°C temperature range, the space shuttle vernier thruster with maximum temperatures of 1400°C and a desired life of 1,000,000 seconds, the cruise missile turbine, automotive and other gas turbines, etc. In order to retain sufficient strength at temperatures above 1000°C refractory materials such as molybdenum, tungsten, tantalum, niobium, rhenium or carbon/carbon must be used to fabricate the parts to withstand these temperatures. These materials and their structurally important alloys have notoriously poor resistance to oxidation in the temperature ranges where their strength characteristics are vitally needed. Protection, in the form of coatings, from the oxidizing environment is crucial for achieving the goals of the aforementioned programs.

Currently the only effective materials available for oxidation protective coatings are silicide-based. These materials are not without their limitations. A phenomenon called "pest behavior" has been observed for silicides. At high and low temperatures these materials have good oxidation resistance, however, in intermediate temperature regions they often disintegrate in air. Additionally, due to the difference of coefficient of expansion between the silicide and the base metal, repeated temperature cycling results in cracking of the coating which allows oxygen to diffuse into the cracks and ultimately destroy the base material. The upper limit for silicide coatings is approximately 1400°C but at these temperatures evaporation of the coating is sufficiently high to limit its life due to the limited thickness available from today's technology.

New oxidation resistant coating materials and processes must be developed which will permit operation in the 500°C to 2000°C temperature range. Not only must these materials survive at these temperatures, but they must last for extended periods of time without evaporating, cracking or spalling. Advancement in the technology of rocket engines and gas turbines depends on the development of these new oxidation resistant protective coatings.

The purpose of the present work was to investigate the chemical vapor deposition (CVD) of Ir, Pt, Rh, ZrO_2 and HfO_2 for the purpose of protecting Re, Mo, Ni, Nb, Cu and carbon composites from oxidation at temperatures from 1000 to 2000°C.

Work immediately preceding this effort, Phase I, had shown that oxidation resistant coatings of iridium and hafnia (HfO_2) could be chemically vapor deposited on several refractory metals (Refs.1,2,3). Preliminary data showed that iridium was

1

particularly promising. A rhenium specimen coated with 50 um (2 mil) of Ir showed no loss of material after 20 minutes exposure to air at over 1800°C. However, the CVD process still needed improvement and optimization. Carbonaceous residues codeposited with the iridium. To achieve a tight coating required heating the deposit to the melting point of iridium, 2410°C, which is a difficult and, in many applications, an unacceptable procedure. An improved method of depositing iridium without codepositing carbon was sought in Phase II and this was achieved through a combination of appropriate reaction gas, pressure and temperature. The iridium deposition process developed here was applied in the fabrication of several rhenium thrusters. Some of these have already been test fired by Aerojet TechSystems using MMH/NTO propellant. One chamber has completed over 8 hours of operation, including over 3600 starts and 4 hours burn time between 2150 and 2200°C at a mixture ratio of 1.65. No measurable change in throat diameter was observed and the weight loss was only 0.9 g or 1.4%.

Iridium has also been applied successfully to molybdenum, tungsten, graphite, carbon composite, niobium, nickel and copper, although the latter three require extra processing.

Deposition of Pt and Rh has not proved as successful as Ir. "Mirror" coatings, tens of nm thick, are readily obtained but nothing approaching the tens of μm (~1 mil) required for an impermeable coating, even over several hours. Consequently, no useful information on the oxidation resistance of Pt & Rh CVD coatings was obtained.

Oxidation rates of bulk hafnia, zirconia, iridium, rhodium, and platinum in moving air were obtained for temperatures from 1100°C to the melting points.

CHEMICAL VAPOR DEPOSITION

Chemical Vapor Deposition (CVD) has been employed for providing coatings for more than a century, but is only recently that this technique has left the laboratory to become a production tool. CVD is a method of plating which relies on the chemical reaction of a vapor at a surface to form solid structural deposits. Since this is done on an atom-by-atom basis, impurity levels are typically less than 0.1% and densities are 99.9%. The process of chemical vapor deposition relies on utilizing a gaseous compound of the element to be deposited which is then flowed over a heated substrate, resulting in thermal decomposition or reduction of the gaseous compound, and subsequent deposition of the material onto the substrate. The first layer forms at nucleation sites, and when the substrate is fully coated, growth continues on the crystal faces of the deposit. Successful CVD (dense, adherent coatings) depends on

experimentally determining the optimum deposition parameters. These parameters include the gaseous compound of the material to be deposited, the substrate temperature, gas concentration, flow, pressure and geometry within the reaction chamber, and substrate material. For the coating to have high integrity and adhesion to the substrate, the substrate must have a similar coefficient of expansion to that of the deposited material or else form a strong chemical or metallurgical bond with it. The thinner the coating the less similar the coefficients of expansion need be. Where coating and substrate form no intermetallic bond and have widely differing coefficients of expansion, a good bond can often be achieved by having a thin interlayer of a third material.

The essential requirements of a CVD facility are that the substrate be maintained at the correct temperature and the plating gases be supplied in the correct ratio and at the correct pressure. The substrate is typically heated resistively, inductively or in a hot wall furnace. The composition of the plating gases is determined by the type of reaction to be used. These include decomposition and reduction. The same material may be deposited using different compounds and different reactions at different temperatures resulting in different microstructures. Compounds can be deposited by simultaneous codeposition of the appropriate elements. The precursor or plating compound must be volatile at the temperature at which it reacts to form a deposit. However, at normal temperature it may exist in the form of a compressed gas, a volatile liquid or a solid which sublimes. These compounds may be purchased or prepared ahead of time, or they may be made in-situ as required, for instance by chlorinating metal shavings or pellets.

The plating compounds used in depositing platinum group metals are solids in the form of powder. The schematic of a typical CVD apparatus for depositing iridium is shown in Figure 1. The iridium source is iridium acetylacetonate which is commercially available. This powder is heated in the horizontal arm of the glass chamber by means of electric resistance heaters. The carrier/reaction gases sweep the sublimed Ir ac-ac vapor past the part to be coated, which is heated with a 450 kHz magnetic field. Finally the reaction products are exhausted.

MATERIALS INVESTIGATED

HAFNIA AND ZIRCONIA

The contract called for measuring the oxidation resistance of bulk HfO_2 and ZrO_2 as a baseline of comparison with CVD coatings of the same composition.

A muffle furnace for oxidation testing of HfO_2 and ZrO_2 at high temperature was constructed. The mantle was Al_2O_3 which
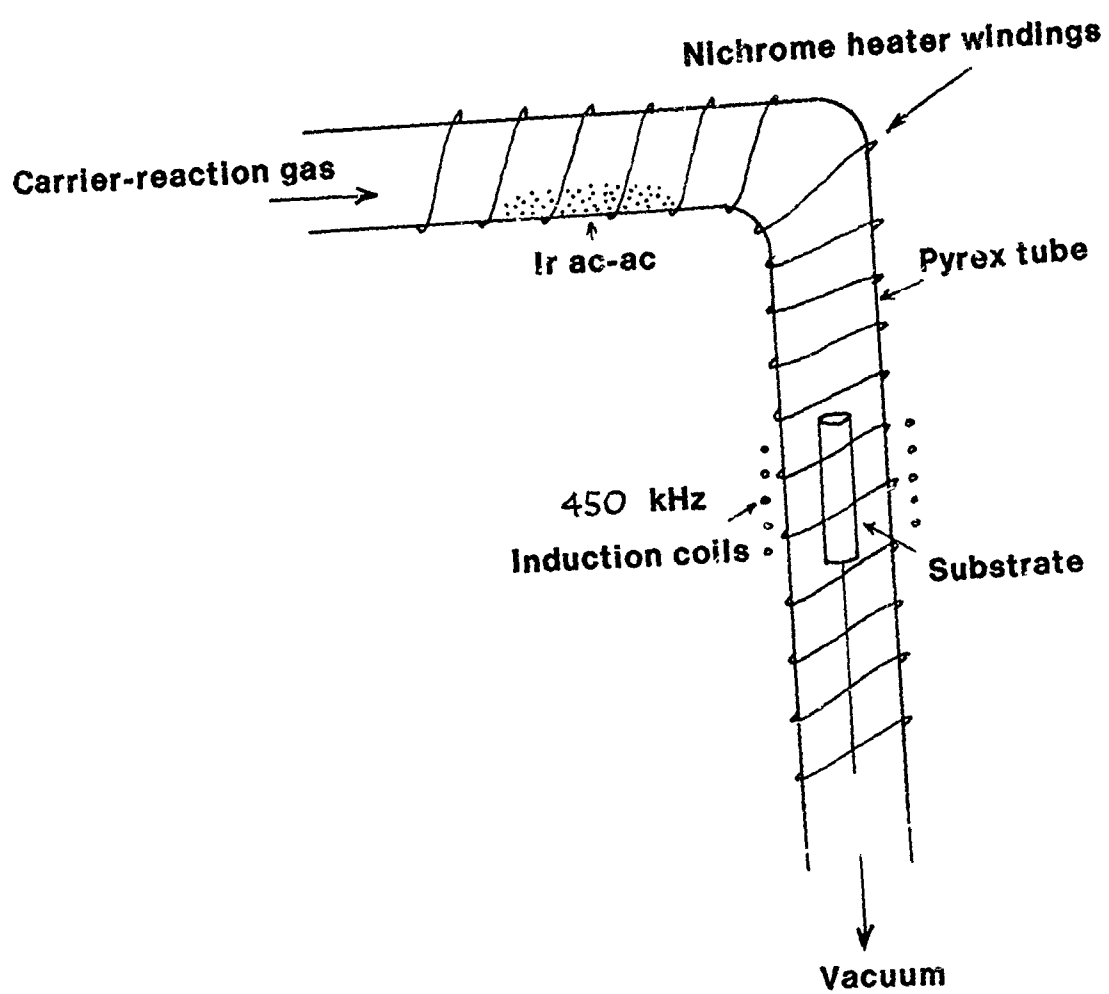
Figure 1. Schematic of CVD apparatus for iridium

4

proved to be useful only to about 1900°C. (At 2000°C a HfO_2 specimen fused to the mantle and a hole formed.). A 2.5 g irregular chunk of sintered pure HfO_2 was maintained in air at 1850-1870°C for one hour with a resultant weight change of -5 mg. The material appeared unchanged as a result of the treatment. However, the same procedure with ZrO_2 resulted in the spontaneous fracture of the specimen into several pieces, and some powder. The scattering of material prevented a significant measurement of weight change. Since the ZrO_2 was unstabilized, an inversion in crystal structure occurred between 800 and 1200°C. This inversion causes a disastrous volume change (about 9%) (Ref.4), which accounts for the fragmentation observed. Hafnia also undergoes crystalline inversion, but the temperature is much higher 1700-1800°C and the associated volume change is 3-4%. The phase inversion can be inhibited by adding small amounts of calcia, magnesia or yttria to the hafnia or zirconia prior to sintering with only small reduction in melting point.

CVD Coatings

HfO_2 coatings on molybdenum were produced by CVD deposition from the chloride in the presence of water vapor. This contrasts with the generated oxide process employed in Phase I - making HfC by CVD, followed by oxidation. The coatings thus formed were grey in color, not white as would be expected for pure HfO_2. However, they are adherent and dense. Once coated the specimen was heated in air for 60 minutes including a plateau of 1400°C for 40 minutes. During the heating there was no visible sign of oxidation (spalling of the surface or smoking). The specimen was examined after cooling, and the tip region, which had been the hottest, was found to be white and powdery. The powder easily flaked off. The molybdenum underneath was discolored but not significantly attacked.

Early on it became clear that CVD coatings of unstabilized ZrO_2 or HfO_2 would not withstand temperature cycling above the respective crystal inversion temperature no matter how well they adhered to a substrate. Because the current effort did not include a study of stabilization, and because such a study was about to begin here under separate sponsorship, the unstabilized hafnia and zirconia coating effort was discontinued.

PLATINUM GROUP METALS

The oxidation resistance of bulk Ir, Rh and Pt was experimentally determined for comparison with CVD coatings of the same metals.

The procedure for this task was to heat a .25 mm (10 mil) diameter wire to various high temperatures by passing an electrical current through it. The wire was enclosed in a quartz

mantle to guard against drafts and to conduct the desired air flow, 10 mm/s past the glowing wire. The mantle diameter of 60 mm is sufficiently large to permit diffusion of reaction products away from the wire and to remain cool enough to condense them. Wire temperature was measured with an optical pyrometer. There was some variation in temperature along the length of the wire; the peak temperature was monitored. The emissivity of a wire was determined by slowly increasing the current until the wire melted, and noting the brightness temperature of the solid at this known temperature, Table 1. This emissivity value was employed to compute true temperature below the melt point. Ir, Rh, and Pt oxidize by forming volatile oxides. Hence the recession of the wire proceeds linearly with time. Oxidation was determined by periodically removing the wire and measuring its diameter.

TABLE 1

Emissivities of Solid Ir, Rh and Pt in air at the Melting Point

	Ir*	Rh*	Pt
Melting Point (accepted value), $^{\circ}$C	2410	1965	1772
Brightness Temperature (.65μm), $^{\circ}$C	2100	1705	1555
Emissivity @ MP (.65 μm)	.34	.27	.28

*Kuriakose (Ref.5) reports the emissivity of Ir and Rh at the melting point in He-O_2 mixture to be 0.42+/-.02 and 0.26-.30 respectively. However, the experimental conditions are somewhat different.

The results are given in Figure 2. In Figures 3, 4 and 5 the results are compared with the data of Krier and Jaffee (Ref.6) and Kuriakose (Ref.7). The air flow velocity used here is that used by Krier and Jaffee. They used preheated air in a narrow chamber. The hot walls reflect back reaction products to the wire. Kuriakose used large diameter chambers with cooled walls which condensed the reaction products, removing them from the oxidation zone; however he employed much higher gas speeds. The cool walls and low velocity of our apparatus should produce oxidation rates intermediate between those of Krier and Kuriakose, wherever the data overlap.
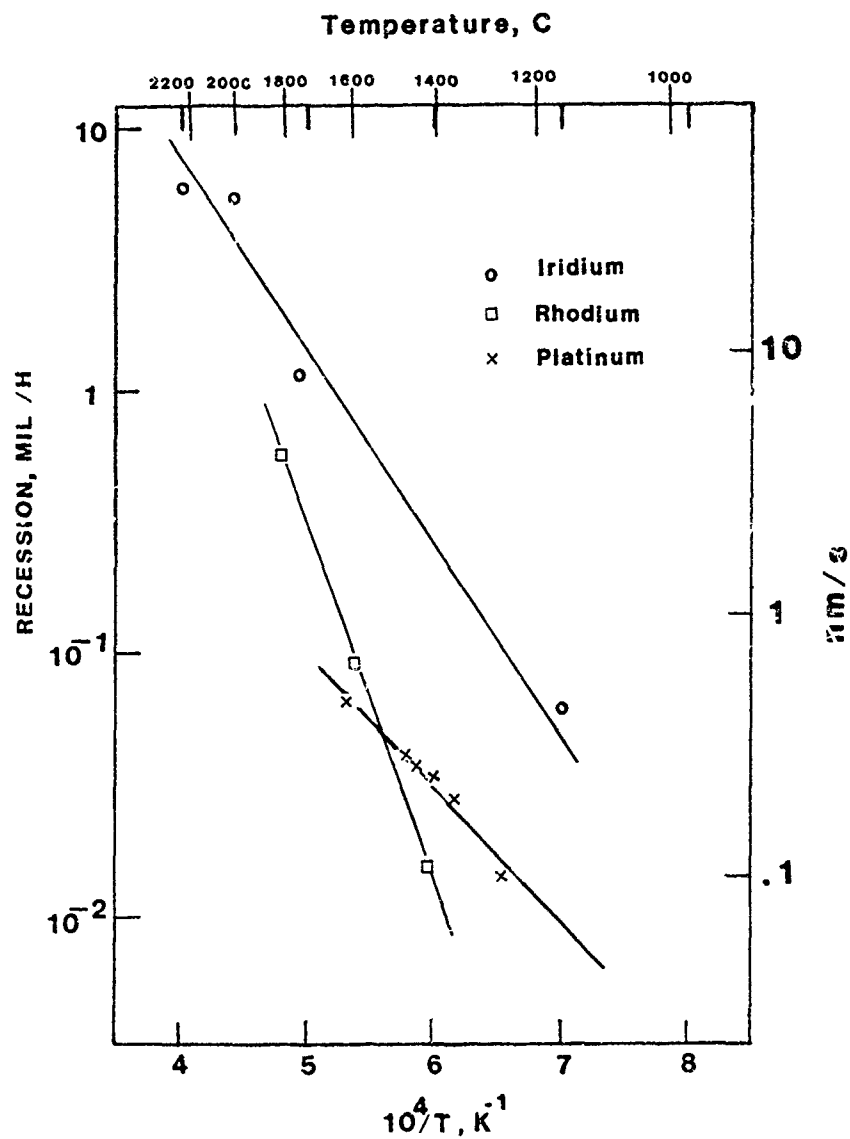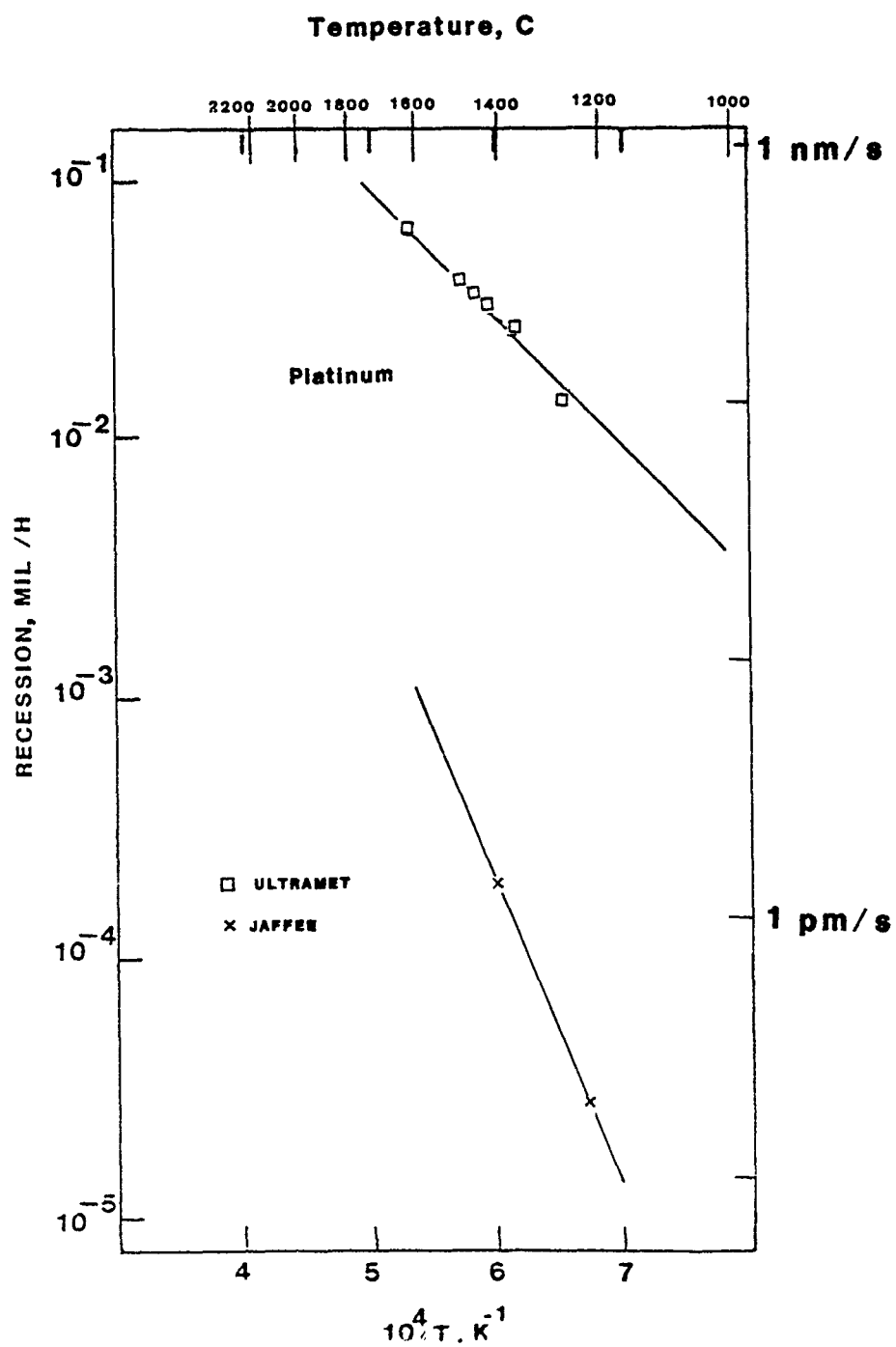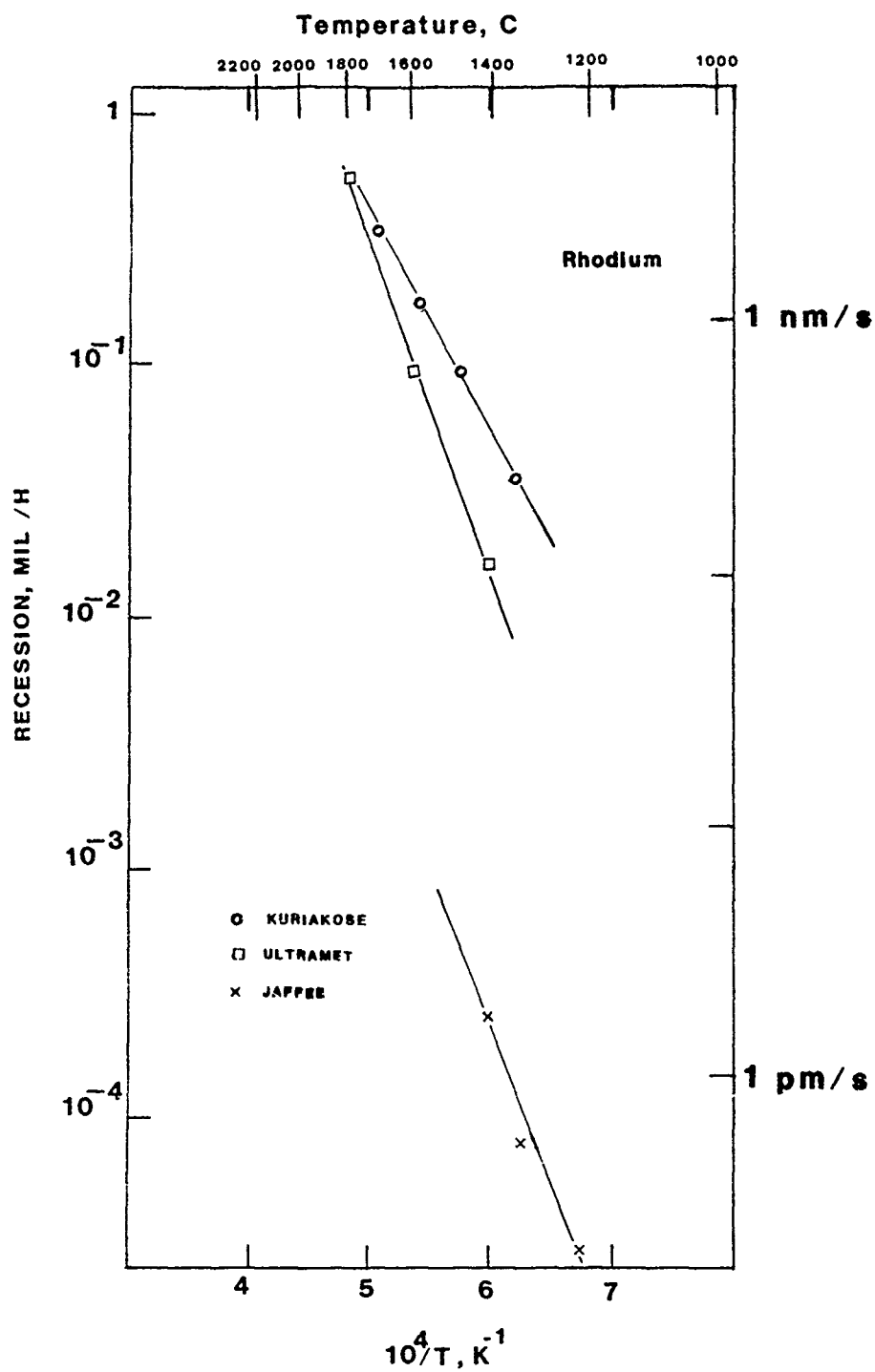
Figure 2.   Oxidation rates of Pt group metals

7

Figure 3.   Comparison of Pt recession rates

8

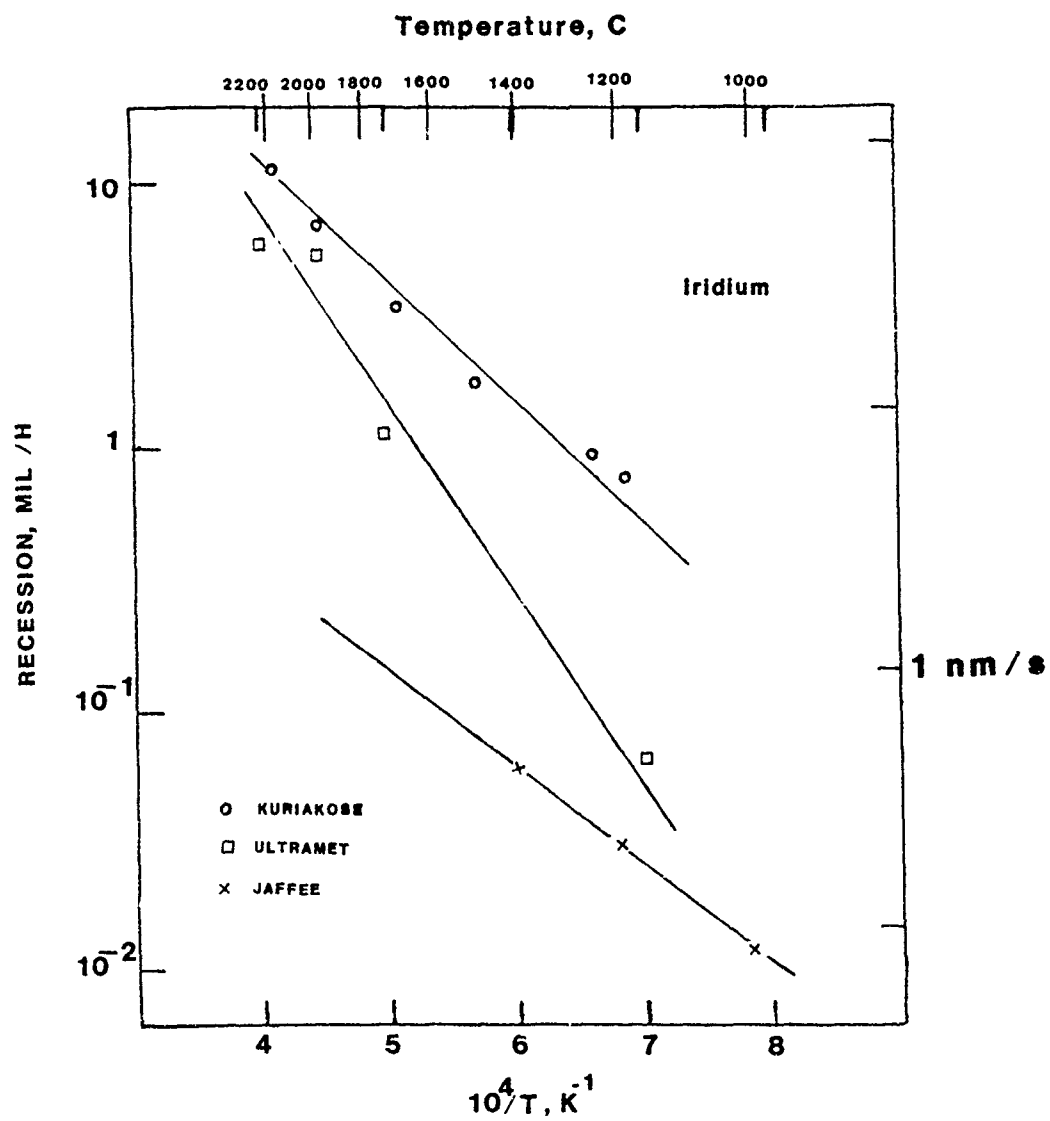Figure 4.   Comparison of Rh recession rates

Figure 5.   Comparison of Ir recession rates

10

CVD Coatings

In any CVD process, the first step is to choose the starting compound (precursor) of the desired metal. The considerations are volatility at temperatures below decomposition, efficiency (what fraction of the metal in the compound ends up depositing on the substrate), reaction (substrate) temperature, and rate of deposit build-up. Metal halides are frequently employed, but for the platinum group metals the volatilization and decomposition temperatures are too close to be useful. Metal organic compounds alleviate this problem and have been shown to produce high purity iridium deposits (Ref.8).

In Phase I we showed that the organometallic compound, iridium (III) 2,4-pentanedionate, $Ir(CH_3COCHCOCH_3)_3$ (also called iridium acetylacetonate or iridium ac-ac for short) satisfied the requirements for depositing iridium. It yields over 50% efficiency, and the portion of the plating gas which doesn't decompose condenses downstream where it can be collected and reused. This is a particularly valuable property considering the cost of iridium. Deposition rates of the order of 7 nm/s (1 mil/hour) are attainable and the deposition temperature is well below $1000^{\circ}C$, compatible with most substrates.

The problem with Ir ac-ac is that it decomposes in vacuo to an iridium with substantial carbon content, the carbon arising from decomposition of the organic ligand. Coatings thus formed become porous when exposed to air at high temperature. Tight coatings were obtained by post deposition heat treatment to $2410^{\circ}C$, the melting point of iridium. This is a cumbersome procedure, and is inapplicable to substrates which melt below $2410^{\circ}C$.

Accordingly a search was made for a combination of pressure, temperature and reaction gas which would avoid codeposition of carbon. This proved possible. Codeposition of carbon has been successfully suppressed, such that electron dispersive X-ray microprobe analysis (windowless) reveals no trace of carbon in the coatings thus prepared (Ref.9).

Other Precursor Compounds Iridium acetylacetonate is a member of the class of metal B-diketone chelates, which are notable for their pronounced volatility. Even more volatile are complexes of substituted acetylacetones including trifluoro pentanedionate (tfa): $(CH_3COCHCOCF_3)^-$ and hexafluoro pentanedionate (hfa): $(CF_3COCHCOCF_3)^-$.

We attempted to obtain all these compounds of Ir, Rh, and Pt. The ac-ac compound is readily available for all three metals. Attempts to produce Ir tfa and hfa proved impractical. The preparation of Ir hfa has been reported in the chemical literature (Ref.10) but the yield was only 10%. Pt hfa, Rh hfa

11

and Rh tfa are available.

The first step in investigating the suitability of these compounds was to measure their volatilities. This was done by vacuum sealing various amounts of compound into glass ampules, heating each to the point where all solid has vaporized and then calculating the pressure from the ideal gas law. The results for vapor pressure vs temperature are shown in Figure 6. It is evident that the volatility increases with the degree of fluorine substitution.

The next step is to determine the temperature range over which heterogeneous phase decomposition of the compound to the metal occurs. In order to avoid decomposition of the compound in-situ, it is necessary that an appreciable difference exist between the temperature where volatility becomes significant (several torr of pressure) and the decomposition temperature. It was found that the volatility of the substituted complexes is accompanied by an offsetting decrease in thermal stability. It is not clear that they offer any advantage over the simple acetylacetonate compounds, except for those applications where lower deposition temperatures are required.

Deposition of Platinum and Rhodium

Platinum and rhodium proved difficult to deposit. A "mirror" coating some tens of nm thick develops in minutes but this did not continue to build up. It appeared that only a small portion of the plating gas encountered the intended substrate. Instead coatings developed on the reaction chamber itself between the plating source and the substrate. Although the distance between source and substrate was minimized and reaction gases were introduced just upstream of the part, acceptable deposition rates have not yet been achieved.

Preoccupation with the easier yielding iridium deposition technology diluted our efforts on Pt and Rh. By no means have approaches been exhausted. Further effort on CVD coatings of Pt and Rh are warranted both because of the success with Ir which is chemically similar and because Pt and Rh are more abundant.

Fluidized Bed Evaporator In order to minimize the residence time of the precursor compound in the evaporator region, and thus reduce in-situ decomposition, a fluidized bed evaporator was developed, Figure 7. There are two important characteristics of fluidized beds which are desirable for this application.

In a static bed, net evaporation occurs only at the surface. Buried particles are hot but are in thermal equilibrium, merely exchanging molecules with one another. In a fluidized bed, evaporation occurs throughout the volume of the bed because every particle is exposed to the carrier gas. Accordingly, particle residence time in the bed is short and high evaporation rates
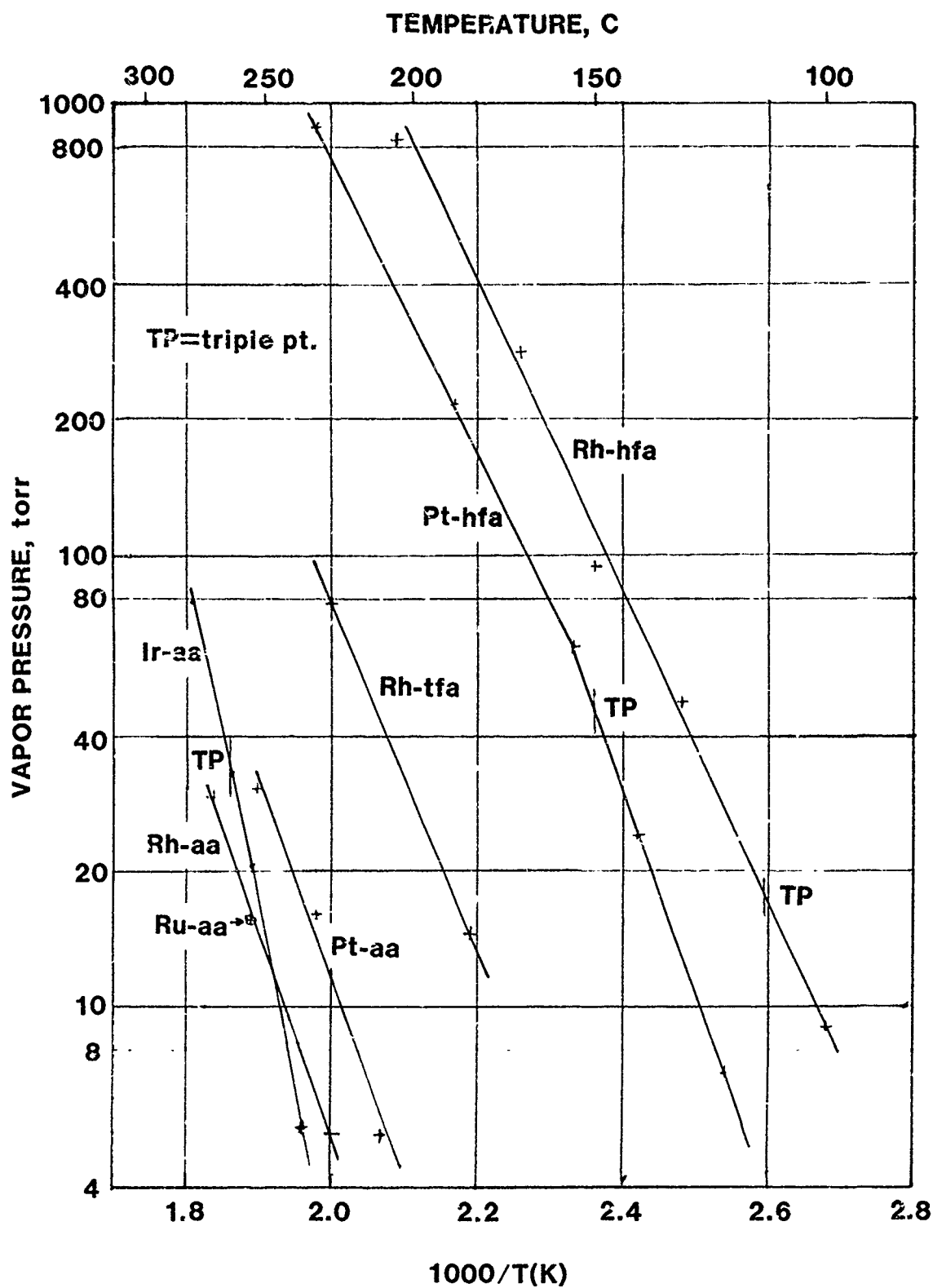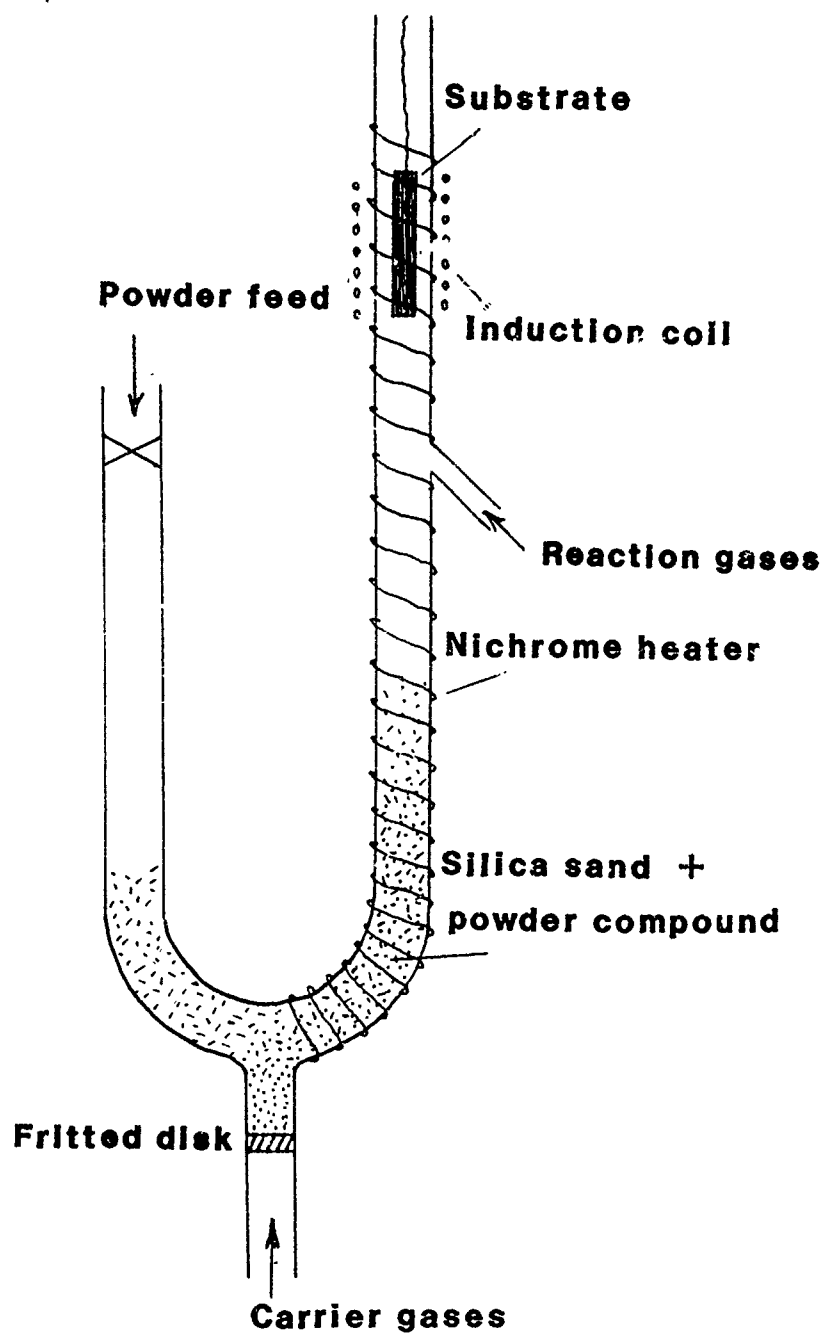
12

Figure 6. **Vapor pressure of Pt group compounds**

13

Figure 7.   **Fluidized bed reactor**

result.

Secondly, the high thermal conductivity of the bed results in rapidly bringing reactants up to temperature with no localized overheating, and consequent decomposition. When a volatile solid is fed into such a bed, evaporation is so rapid that the equilibrium vapor pressure is attained over a wide range of carrier gas flows. Thus the mass flow rate of the _vapor_ is determined by its vapor pressure and the carrier gas flow.

A problem has been the carryover of fines. The ablating powder grains reach a size where they can be entrained in the gas stream. Fines appear to account for 30-40% of the total transport of Ir ac-ac. If the fines are not trapped and some strike the substrate, the quality of the deposit is degraded.

The stationary bed shown in Figure 1 has proved adequate for the coating of experimental specimens and 1-2 cm diameter nozzles, but the fluidized bed will be more efficient and convenient for coating larger parts.

Deposition of Iridium

The use of organometallics as precursors in the chemical vapor deposition of platinum group metals is not new. Powell mentions acetylacetonates and cyclopentadienyl (metal-ocene) compounds as promising with regard to Pt and Pd (Ref.11). The codeposition of carbonaceous residues, which we encountered with Ir ac-ac in Phase I, are noted with regard to Pd ac-ac. It is claimed that these can be suppressed by the addition to the plating vapor of an oxidizing agent such as carbon dioxide.

In this task we investigated the deposition parameters of Ir ac-ac. The independent variables are:

- carrier/reaction gas composition
- carrier/reaction gas temperature
- carrier/reaction gas flow rate
- total pressure
- substrate temperature
- reaction chamber geometry

The plating gas is generally at saturation so its pressure is determined by the carrier gas temperature. The total pressure is controlled by means of the exhaust pumping rate. The carrier gas flow rate and chamber/substrate geometry determines the velocity of the gases past the substrate.

In general, we have found that good coatings are obtained at pressures near 1 atm. This is convenient and most deposits have been made at 1 atm. Lower pressures have been investigated. At about 80 kPa absolute a problem called "cornflaking" has been encountered. The coating comes loose in the form of a myriad of

curved flakes one edge of which remains attached to the substrate. Presumably severe internal stresses lead to this condition. Lower deposition pressures have not been thoroughly explored. Since most organometallics function well at plating pressures of a few torr, this regime merits further work. Although it seems that reducing plating gas concentration should reduce plating rates, other factors such as reduction of the boundary layer, and suppression of gas phase nucleation (which permits higher substrate temperature) can sometimes more than offset the concentration effect.

With regard to the reaction gas, several gases were tried including carbon dioxide, carbon monoxide, hydrogen, methane and oxygen. A certain mixture of these gases eliminates the carbonaceous deposits and results in deposits of theoretical specific density, 22.4, as compared to 6-10 without the reaction gases.

Argon, nitrogen and other inert gases have been employed as a carrier gases. When used in conjunction with the reaction gas, each has a moderate effect on reducing the deposition rate. Flow rates can be varied over wide ranges with important but opposite effects on efficiency and coating uniformity.

SUBSTRATES INVESTIGATED

The objective of this task was to prepare a design table indicating the most effective oxidation resistant coating for each substrate, the optimal deposition parameters, and appropriate coating thicknesses. Hafnia and zirconia proved unsuitable for all substrates because of the phase inversion of unstabilized HfO_2 and ZrO_2, as well as the brittleness. Platinum and rhodium could not be deposited in sufficient thickness to protect against oxidation. This left only iridium.

Fortunately we can apply iridium to all the specified substrates - Re, Mo, Ni, Nb, Cu and carbon/carbon composites. Re, Mo and W are simple to coat. Adhesion is good without any special precautions (other than careful surface cleaning). The others require certain initial procedures. Iridium deposited on Ni, Nb, and Cu does not adhere unless the coating is less than about ten microns thick. This is not surprising in the cases of Ni and Cu which have large thermal coefficients of expansion relative to Ir. Nb is often difficult to bond to because it is so reactive. Acetylacetone, which is probably the reaction product in the iridium ac-ac CVD process, has been observed to attack Cu at room temperature. In any event, success with bonding Ir to all three metals has been achieved.

Carbon composites (and graphite) have been coated directly with iridium, but employing an initial coating of W or Re

promotes bonding.

Occasionally delamination occurs in the form of an array of peeled back flakes attached at an edge. This "cornflaking" can occur both before and after heat treatment. Cornflaking is generally associated with too rapid deposition, and frequently occurs at the first point of impingement of the plating gas stream on the part, particularly if the surface there is perpendicular to the impingement. Fines may be a culprit in the case of normal impingement. Remedies include placing a shield or "hat" to prevent direct impingement, and reducing the deposition temperature and Ir ac-ac concentration.

Delamination also occurs as blisters in an unbroken coating. It seems to be minimized by maintaining deposition conditions constant during a run, and particularly by not stirring up particulates in the bed. We have observed tiny voids decorating the deposit at a depth correlated with agitation of the Ir ac-ac bed during deposition. This line of voids sometimes defines where delamination occurs in a blister. There is still concern that whatever causes the blisters is still continuously present and does degrade the deposition, but is not disastrous unless it occurs in bursts.

With appropriate precautions, defects in the coating can be avoided. Dense adherent non-porous coatings are now routinely achieved.

Oxidation Resistance of Iridium Coated Substrates

Representative samples of the iridium coated substrates were evaluated for oxidation resistance by heating in freely convecting air at temperatures up to 1900°C. The samples, in the form of 3 mm or 6 mm rods or tubes were mounted horizontally so the ends (and interior) were protected by argon, and the central region was heated inductively. See Figure 8 for the experimental arrangement. The part was monitored visually for signs of smoking, cracking or erosion of the coating. The quantitative measure of oxidation is mass loss, which was determined by stopping the test periodically, allowing the sample to cool, and weighing it. Metallographic examination of selected specimens was made.

A typical test result is shown in Table 2. Here a 32 mm x 3 mm dia. rhenium tube, which was coated with 9 layers of Ir to a thickness between 105 and 125 μm, was tested in three runs. The total weight of the coating was 800 mg. After testing, the coating was examined microscopically. There were no pinholes or cracks. About 40 μm of coating was removed during oxidation.

17
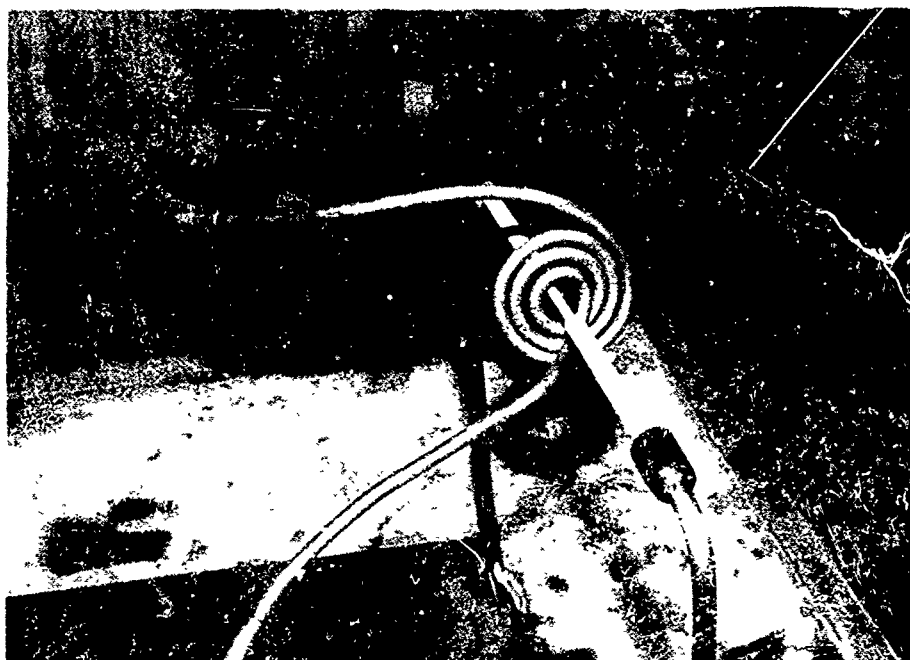
Figure 8.   Oxidation apparatus

TABLE 2

Run #	Temp, $^\circ$C	Duration, h	Mass loss, mg
1	1510	2	35
2	1510	3	57
3	1870-1690	2	56

Iridium coatings on molybdenum and tungsten behave similarly to rhenium with respect to oxidation. Coatings up to at least 100 µm in thickness withstand temperature cycling to 2000°C without loss of adherence and appear to be impermeable to oxygen.

Surface reactions occur between iridium and copper, nickel and niobium. Special precautions must be taken at the onset of deposition to promote bonding. At elevated temperatures there is evidence of rapid diffusion of all three of these metals through the iridium coating. In the case of copper, a pink color develops at the iridium surface after only a few minutes at 900°C. At temperatures within the limits of their mechanical strengths iridium provides excellent oxidation protection for all three. Thus at 450°C for copper and nickel, there is no change in appearance in the iridium surface nor any measurable weight loss (<1 mg). Iridium protects niobium from oxidation to at least 1000°C, where surface discoloration is observed but not a significant weight loss.

Iridium has also proved effective in protecting graphite and carbon/carbon composites from oxidation. Thick coatings tend to spall indicating reduced bonding energy. This has been overcome by employing an interlayer of rhenium or tungsten which bond well to carbon and iridium. The surface imperfections and anisotropy of carbon composites have stood in the way of routine success in achieving tight coatings under temperature cycling. Further exploration of interlayers to improve bonding are warranted by the prospective payoff.

What these results demonstrate is that iridium coatings make it possible to employ the subject materials, except perhaps for carbon, at temperatures limited only by their mechanical properties, not by oxidation considerations.

FABRICATION OF IRIDIUM COATED RHENIUM THRUSTERS FOR AEROJET

An unparalleled opportunity arose for a practical demonstration of oxidation resistant iridium coatings on an actual engine component. Ultramet had previously fabricated a rhenium thruster by means of CVD for Aerojet TechSystems. This is a 22.3 N (5 lbf) thrust, 73 mm (2.9 inch) length nozzle whose configuration is shown in Figure 9. This unit had been test

DIMENSIONS IN MILLIMETERS

Figure 9.   Aerojet test chamber configuration

fired using MMH/NTO (monomethyl hydrazine/nitrogen tetroxide). A typical test program generally consists of starting at fuel rich oxygen/fuel mixture ratios (MR) and conducting a series of 100 to 300 second tests in which the MR is increased until some material loss is noted. A series of 1000 second tests are then conducted at MR's slightly below the threshold of wall regression. Mass and dimensional changes are recorded following each 1000 second burn. The final series of tests are pulsing durability tests. Each test comprises 300 to 6000 on-off cycles. Dimensional and/or weight inspections follow each test group. Test results led to the following conclusions.

- Uncoated rhenium can operate at steady-state up to a MR of 1.5 and ~2065°C (3750°F) without material loss. Measurable regression was observed in the optimum performance range of MR 1.65 to 2.0.
- Uncoated rhenium is unsuitable for extensive (greater than several hundred) pulsing cycles because uncontrolled start and shut down transients result in material oxidation. The loss rate in pulsing is not significantly influenced by MR and temperature over the test range, 1370 to 2040°C (2500 to 3700°F).
- No material loss was observed in any testing (steady-state and pulsing) when the operating temperatures were below 1590°C (2900°F).

Aerojet was very interested in demonstrating improved thruster performance by extending the operating regime of the thrusters to higher temperatures and mixture ratios. Clearly this requires oxidation protection of the rhenium.

In consultation with the Rocket Propulsion Lab and Aerojet TechSystems, it was decided that the demonstration task of this SBIR program would consist of supplying two iridium coated rhenium nozzles to Aerojet for test firing.

The nozzles were entirely produced by Ultramet using chemical vapor deposition and a novel integrated fabrication technique. Coating the inside of a long chamber presents obvious inspection problems, especially during deposition. Instead, we started by depositing a nominal 40 μm iridium coating on a molybdenum mandrel which conformed to the ID specification of the nozzle. After assuring ourselves that the coating was defect free, we deposited 1 mm of rhenium on top of the iridium, thus forming the main structure of the nozzle. To complete the fabrication, the ends were cut to length and the molybdenum mandrel was chemically dissolved out. leaving a free standing nozzle. Firing tests of the first nozzle revealed that reaction products in the exhaust severely attack the external surface of the nozzle, so an iridium coating was applied over the rhenium. The second nozzle was fabricated with both an inner and outer surface of iridium.

Appendix A, issued separately, consists of Aerojet's test

report on the firing of these two iridium coated nozzles. Clearly the goal of extending the operating regime has been achieved. The temperature and MR which can be sustained without material loss has been extended from 2065°C at 1.5 to at least 2200°C at 1.64. Of greater importance is the ability to withstand start-stop transients which has been the determinant of thruster life. In more than 3600 firings to over 1900°C in December 1985, the inside surface of the first thruster lost no measurable material. By comparison about 0.2 mm (.008 inch) of rhenium would have been lost in similar tests of an unprotected chamber. This chamber has now completed over 8 hours of operation without visible evidence of liner degradation. Tests 155 to 186 (following the application of iridium to the outer surface) accumulated almost 8 hours between 2100 and 2230°C and resulted in a loss of 0.9 g or 1.4%.

The second chamber failed after 3.5 hours of operation, when a small hole developed near the throat. It is important to note that this hole originated on the outside and developed inward due to attack by the reaction products in the nozzle exhaust. There appeared to be defects in the outer coating which did not occur with the heavier coating on the first chamber. This appears to be due to a mistake in the procedure and not an intrinsic problem. Even so an uncoated rhenium nozzle would not last more than a few minutes under the same conditions.

CONCLUSIONS AND RECOMMENDATIONS

Chemically vapor deposited coatings of iridium have been shown to afford a high degree of oxidation protection to a variety of metals and carbon. When properly prepared, these coatings are adherent and impermeable to oxygen; they appear to be limited only by the melting point (2410°C) and by recession of the iridium due to the slow formation of a volatile oxide.

Application of this new technology to an actual engine component, an iridium coated rhenium thruster nozzle for spacecraft station keeping, has resulted in both enormously extended lifetime and greatly enhanced performance. No longer is it necessary to operate the nozzle at suboptimum temperatures and oxidizer/fuel mixture ratios on account of oxidation considerations. With an iridium coating, full advantage can be taken of the excellent mechanical strength characteristics of rhenium at elevated temperature.

There are two directions for extending this work. One is to apply the technology to other systems where susceptibility to oxidation or corrosion limits performance. Another is to study the deposition process for Pt group metals further in order to get even better protection than demonstrated herein.

In the first category are other engine components including carbon composites, graphite, niobium alloys. Also included are instances where a thin coating of iridium on an inexpensive substrate can substitute for a bulk precious item such as Pt crucibles, or sputtering targets.

In the second category are perfecting Pt and Rh deposition, codeposition of Pt group metals to form alloys, codeposition of Pt group metals and transition elements to form the ultra stable Engel-Brewer compounds, as well as the more prosaic tasks of making iridium deposition more reliable and defect-free and moving it out of the laboratory into a commercial process. It should be noted that the alloys and compounds offer great promise for reducing the recession rate of the coatings and for extending protection temperatures to above 2410°C, the melting point of iridium.

Under separate contract Ultramet has demonstrated that a thick HfO_2 coating over iridium reduces the recession rate of the latter by a factor of 20 in air at 2000°C. Although the hafnia cracks due to differential expansion, it has remained adherent. It cannot be relied on for primary oxidation resistance but it can prolong the life of an iridium coating (Ref.12).

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